PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : D06M 16/00, D06L 3/02, C11D 3/386, D06P 5/02 — A1

(11) International Publication Number: WO 97/25469

(43) International Publication Date: 17 July 1997 (17.07.97)

(21) International Application Number: PCT/DK97/00003

(22) International Filing Date: 8 January 1997 (08.01.97)

(30) Priority Data:
0025/96 12 January 1996 (12.01.96) DK

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(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: TEXTILES BLEACHING/BRIGHTENING

(57) Abstract

This invention deals with a process for providing a bleached and brightened look in the colour density of the surface of dyed fabric, the process comprising: (a) contacting, in an aqueous medium, a dyed fabric with a phenol oxidizing enzyme system and an enhancing agent; (b) simultaneously or subsequently treating said fabric with a brightening agent.

TEXTILES BLEACHING/BRIGHTENING

FIELD OF INVENTION

The present invention relates to a process for providing a bleached and brightened look in the colour density of the surface of dyed fabric, especially cellulosic fabric such as denim.

BACKGROUND ART

The past several years have seen the emergence of a new industry, the so called "jeans stonewashing" segment, generated by the fashion demands of a generation desirous of stylish, but informal and comfortable clothing.

Originally, all of the indigo jeans on the market were stiff and uncomfortable when first purchased, due to the finishing system used for denim fabrics.

The first step in the processing evolution was to sell jeans that had been laundered by the manufacturer. These "pre-washed" jeans had a slightly faded appearance and a softer hand that felt comfortable, as though they had been laundered several times. This trend became fashionable as well, and consumers were willing to pay the extra cost involved for this additional processing.

Not long after the introduction of pre-washed jeans, the idea of using abrasive stones to accelerate the aging process was developed, and "stone washing" became the second step in the evolution. Volcanic stones were included in the wash, or tumbled with the damp garments to wear down the stiffest portions such as belt areas, cuffs, and pockets. However, the use of stones to abrade jeans is very destructive to equipment, so today the stones are often substituted with a cellulase treatment, or a combination of stones and cellulase is used to achieve the worn look (for reference see "AATCC:

Garment Wet Processing Technical Manual", 1994, published by American Association of Textile Chemists and Colorists, pp. 19-21).

The third evolutionary step in the indigo jeans area was the introduction of the hypochlorite bleach following the stone washing process, whereby a new, lightened bluejean family resulted. The chlorine process, however, is unwanted from an environmental point of view; alternatives, such as a H_2O_2 bleach, have been tried but the pH value has to be very high in order to achieve the desired effect; this is a disadvantage both from an environmental and from an economic point of view.

Bleaching enzymes such as peroxidases together with hydrogen peroxide or oxidases together with oxygen have also been suggested for bleaching of dyed textiles, either alone or together with a phenol such as p-hydroxycinnamic acid, 2,4-dichlorophenol, p-hydroxybenzene sulphonate, vanillin or p-hydroxybenzoic acid (see WO 92/18683). The disclosed process is not efficient, but we have found that by using other enhancing agents the process can be made efficient, but the fabric will get a greyish/yellowish look normally unwanted by the customers.

Thus there is still a need for an environmental acceptable process which can give the denim the desired bleached and brightened look.

SUMMARY OF THE INVENTION

Surprisingly it has been found that by carefylly selecting the type and dosage of brightening agent it is possible to create a very efficient process for providing any look and shade between that of fabric enzymatically bleached and that of fabric traditionally brightened with hypochlorite, the process comprising

(a) contacting, in an aqueous medium, a dyed fabric

with a phenol oxidizing enzyme system and an enhancing agent;

(b) simultaneously or subsequently treating said fabric with a brightening agent.

DETAILED DESCRIPTION OF THE INVENTION

Dyed Fabric

The process of the invention may be applied to any dyed fabric known in the art, in particular to syntetic fabrics such as polyester or to natural fabrics.

The process of the invention is most beneficially applied to cellulose-containing fabrics, such as cotton, viscose, rayon, ramie, linen, Tencel, or mixtures thereof, or mixtures of any of these fibres, or mixtures of any of these fibres together with synthetic fibres. In particular, the fabric is denim. The process of the invention may also be applied to other natural materials such as silk.

The fabric may be dyed with vat dyes such as indigo, or indigo-related dyes such as thioindigo. The fabric may also be dyed with more than one dye, e.g., first with a sulphur dye and then with an indigo dye, or vice versa.

In a most preferred embodiment of the process of the invention, the fabric is indigo-dyed denim, including clothing items manufactured therefrom.

Phenol Oxidizing Enzyme Systems

By the term "a phenol oxidizing enzyme system" is meant a system in which an enzyme, by using hydrogen peroxide or molecular oxygen, is capable of oxidizing organic compounds containing phenolic groups. Examples of such enzymes are peroxidases and oxidases.

If the phenol oxidizing enzyme system requires a source of hydrogen peroxide, the source may be hydrogen peroxide or a hydrogen peroxide precursor for in situ production of hydrogen peroxide, e.g., percarbonate or

perborate, or a hydrogen peroxide generating enzyme system, e.g., an oxidase and a substrate for the oxidase, or an amino acid oxidase and a suitable amino acid, or a peroxycarboxylic acid or a salt thereof. Hydrogen peroxide may be added at the beginning of or during the process, e.g., in a concentration corresponding to 0.001-25 mM H_2O_2.

If the phenol oxidizing enzyme system requires molecular oxygen, molecular oxygen from the atmosphere will usually be present in sufficient quantity.

The enzyme of the phenol oxidizing enzyme systems may be an enzyme exhibiting peroxidase activity or a laccase or a laccase related enzyme as described below.

According to the invention the concentration of the phenol oxidizing enzyme in the aqueous medium where the localized variation in the colour density of the surface of the dyed fabric is taking place, may be 0.001-100 mg of enzyme protein per liter, in particular 0.01-10 mg of enzyme protein per liter.

Peroxidases and Peroxidase Acting Compounds

An enzyme exhibiting peroxidase activity may be any peroxidase enzyme comprised by the enzyme classification (EC 1.11.1.7), or any fragment derived therefrom, exhibiting peroxidase activity, or synthetic or semisynthetic derivatives thereof (e.g. porphyrin ring systems or microperoxidases, cf. e.g. US 4,077,768, EP 537,381, WO 91/05858 and WO 92/16634). Such enzymes are known from microbial, plant and animal origins.

Preferably, the peroxidase employed in the method of the invention is producible by plants (e.g. horseradish or soybean peroxidase) or microorganisms such as fungi or bacteria. Some preferred fungi include strains belonging to the subdivision Deuteromycotina, class Hyphomycetes, e.g. *Fusarium*, *Humicola*, *Tricoderma*, *Myrothecium*, *Verticillum*, *Arthromyces*, *Caldariomyces*, *Ulocladium*, *Embellisia*,

Cladosporium or *Dreschlera*, in particular *Fusarium oxysporum* (DSM 2672), *Humicola insolens*, *Trichoderma resii*, *Myrothecium verrucana* (IFO 6113), *Verticillum alboatrum*, *Verticillum dahlie*, *Arthromyces ramosus* (FERM P-7754), *Caldariomyces fumago*, *Ulocladium chartarum*, *Embellisia alli* or *Dreschlera halodes*.

Other preferred fungi include strains belonging to the subdivision Basidiomycotina, class Basidiomycetes, e.g. *Coprinus*, *Phanerochaete*, *Coriolus* or *Trametes*, in particular *Coprinus cinereus* f. *microsporus* (IFO 8371), *Coprinus macrorhizus*, *Phanerochaete chrysosporium* (e.g. NA-12) or *Trametes* (previously called *Polyporus*), e.g. *T. versicolor* (e.g. PR4 28-A).

Further preferred fungi include strains belonging to the subdivision Zygomycotina, class Mycoraceae, e.g. *Rhizopus* or *Mucor*, in particular *Mucor hiemalis*.

Some preferred bacteria include strains of the order Actinomycetales, e.g. *Streptomyces spheroides* (ATTC 23965), *Streptomyces thermoviolaceus* (IFO 12382) or *Streptoverticillum verticillium* ssp. *verticillium*.

Other preferred bacteria include *Bacillus pumilus* (ATCC 12905), *Bacillus stearothermophilus*, *Rhodobacter sphaeroides*, *Rhodomonas palustri*, *Streptococcus lactis*, *Pseudomonas purrocinia* (ATCC 15958) or *Pseudomonas fluorescens* (NRRL B-11).

Further preferred bacteria include strains belonging to *Myxococcus*, e.g. *M. virescens*.

The peroxidase may furthermore be one which is producible by a method comprising cultivating a host cell transformed with a recombinant DNA vector which carries a DNA sequence encoding said peroxidase as well as DNA sequences encoding functions permitting the expression of the DNA sequence encoding the peroxidase, in a culture medium under conditions permitting the expression of the peroxidase and recovering the peroxidase from the culture.

Particularly, a recombinantly produced peroxidase is a peroxidase derived from a *Coprinus* sp., in particular *C. macrorhizus* or *C. cinereus* according to WO 92/16634, or a variant thereof, e.g., a variant as described in WO 94/12621.

In the context of this invention, peroxidase acting compounds comprise peroxidase active fragments derived from cytochromes, haemoglobin or peroxidase enzymes, and synthetic or semisynthetic derivatives thereof, e.g. iron porphins, iron porphyrins, and iron phthalocyanine and derivatives thereof.

Determination of Peroxidase Activity:

1 peroxidase unit (PODU) is the amount of enzyme that catalyzes the conversion of 1 µmole hydrogen peroxide per minute at the following analytical conditions: 0.88 mM hydrogen peroxide, 1.67 mM 2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonate), 0.1 M phosphate buffer, pH 7.0, incubated at 30°C, photometrically followed at 418 nm.

Laccase and Laccase Related Enzymes

In the context of this invention, laccases and laccase related enzymes contemplate any laccase enzyme comprised by the enzyme classification (EC 1.10.3.2), any chatechol oxidase enzyme comprised by the enzyme classification (EC 1.10.3.1), any bilirubin oxidase enzyme comprised by the enzyme classification (EC 1.3.3.5) or any monophenol monooxygenase enzyme comprised by the enzyme classification (EC 1.14.99.1).

The laccase enzymes are known from microbial and plant origin. The microbial laccase enzyme may be derived from bacteria or fungi (including filamentous fungi and yeasts) and suitable examples include a laccase derivable from a strain of *Aspergillus, Neurospora*, e.g. *N. crassa, Podospora, Botrytis, Collybia, Fomes, Lentinus, Pleurotus, Trametes*, e.g. *T. villosa* and *T. versicolor, Rhizoctonia*, e.g. *R. solani, Coprinus*, e.g. *C. plicatilis* and *C. cinereus, Psatyrella, Myceliophtho-*

ra, e.g. *M. thermophila*, *Schytalidium*, *Polyporus*, e.g. *P. pinsitus*, *Phlebia*, e.g. *P. radita* (WO 92/01046), or *Coriolus*, e.g. *C.hirsutus* (JP 2-238885).

The laccase or the laccase related enzyme may furthermore be one which is producible by a method comprising cultivating a host cell transformed with a recombinant DNA vector which carries a DNA sequence encoding said laccase as well as DNA sequences encoding functions permitting the expression of the DNA sequence encoding the laccase, in a culture medium under conditions permitting the expression of the laccase enzyme, and recovering the laccase from the culture.

Determination of Laccase Activity (LACU)

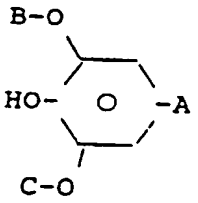
Laccase activity is determined from the oxidation of syringaldazin under aerobic conditions. The violet colour produced is photometered at 530 nm. The analytical conditions are 19 µM syringaldazin, 23.2 mM acetate buffer, pH 5.5, 30°C, 1 min. reaction time.

1 laccase unit (LACU) is the amount of enzyme that catalyses the conversion of 1.0 µmole syringaldazin per minute at these conditions.

Enhancing Agents

According to the present invention an enhancing agent is any compound that enhances the bleaching process. The enhancing agent will typically be an organic compound, e.g., an organic compound described by one of the following formulas:

The enhancing agent may be described by the following formula I:



in which formula A is a group such as -D, -CH=CH-D, -CH=CH-CH=CH-D, -CH=N-D, -N=N-D, or -N=CH-D, in which D is selected from the group consisting of -CO-E, $-SO_2$-E, -N-XY, and $-N^+$-XYZ, in which E may be -H, -OH, -R, or -OR, and X and Y and Z may be identical or different and selected from -H and -R; R being a C_1-C_{16} alkyl, preferably a C_1-C_8 alkyl, which alkyl may be saturated or unsaturated, branched or unbranched and optionally substituted with a carboxy, sulfo or amino group; and B and C may be the same or different and selected from C_mH_{2m+1}; $1 \leq m \leq 5$.

In a preferred embodiment A in the above mentioned formula is -CO-E, in which E may be -H, -OH, -R, or -OR; R being a C_1-C_{16} alkyl, preferably a C_1-C_8 alkyl, which alkyl may be saturated or unsaturated, branched or unbranched and optionally substituted with a carboxy, sulfo or amino group; and B and C may be the same or different and selected from C_mH_{2m+1}; $1 \leq m \leq 5$.

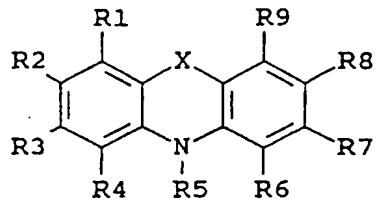
In the above mentioned formula A may be placed meta to the hydroxy group instead of being placed in the para-position as shown.

In particular embodiments, the enhancing agent is acetosyringone, methylsyringate, ethylsyringate, propyl-syringate, butylsyringate, hexylsyringate, or octylsyringate.

The enhancing agents described above may be prepared using methods well known to those skilled in the art; some of the enhancing agents are also commercially available, e.g.,

acetosyringone. Methylsyringate, ethylsyringate, propylsyringate, butylsyringate, hexylsyringate and octylsyringate may be produced as disclosed in Chem. Ber. 67, 1934, p. 67.

The enhancing agent used in the present invention may also be described by the following formula II:



in which formula X represents (-O-) or (-S-), and the substituent groups R^1-R^9, which may be identical or different, independently represents any of the following radicals: hydrogen, halogen, hydroxy, formyl, carboxy, and esters and salts hereof, carbamoyl, sulfo, and esters and salts hereof, sulfamoyl, nitro, amino, phenyl, C_1-C_{14}-alkyl, C_1-C_5-alkoxy, carbonyl-C_1-C_5-alkyl, aryl-C_1-C_5-alkyl; which carbamoyl, sulfamoyl, and amino groups may furthermore be unsubstituted or substituted once or twice with a substituent group R^{10}; and which phenyl may furthermore be unsubstituted or substituted with one or more substituent groups R^{10}; and which C_1-C_{14}-alkyl, C_1-C_5-alkoxy, carbonyl-C_1-C_5-alkyl, and aryl-C_1-C_5-alkyl groups may be saturated or unsaturated, branched or unbranched, and may furthermore be unsubstituted or substituted with one or more substituent groups R^{10};

which substituent group R^{10} represents any of the following radicals: halogen, hydroxy, formyl, carboxy and esters and salts hereof, carbamoyl, sulfo and esters and salts hereof, sulfamoyl, nitro, amino, phenyl, aminoalkyl, piperidino, piperazinyl, pyrrolidino, C_1-C_5-alkyl, C_1-C_5-alkoxy; which carbamoyl, sulfamoyl, and amino groups may furthermore be unsubstituted or substituted once or twice with hydroxy, C_1-C_5-alkyl, C_1-C_5-alkoxy; and which phenyl may furthermore be

substituted with one or more of the following radicals: halogen, hydroxy, amino, formyl, carboxy and esters and salts hereof, carbamoyl, sulfo and esters and salts hereof, and sulfamoyl; and which C_1-C_5-alkyl, and C_1-C_5-alkoxy groups may furthermore be saturated or unsaturated, branched or unbranched, and may furthermore be substituted once or twice with any of the following radicals: halogen, hydroxy, amino, formyl, carboxy and esters and salts hereof, carbamoyl, sulfo and esters and salts hereof, and sulfamoyl;

or in which general formula two of the substituent groups R^1-R^9 may together form a group -B-, in which B represents any of the following the groups: $(-CHR^{10}-N=N-)$, $(-CH=CH-)_n$, $(-CH=N-)_n$ or $(-N=CR^{10}-NR^{11}-)$, in which groups n represents an integer of from 1 to 3, R^{10} is a substituent group as defined above and R^{11} is defined as R^{10}.

In particular embodiments, the enhancing agent is 10-methylphenothiazine, phenothiazine-10-propionic acid, N-hydroxysuccinimide phenothiazine-10-propionate, 10-ethylphenothiazine-4-carboxylic acid, 10-ethylphenothiazine, 10-propylphenothiazine, 10-isopropylphenothiazine, methyl phenothiazine-10-propionate, 10-phenylphenothiazine, 10-allylphenothiazine, 10-(3-(4-methylpiperazin-1-yl)propyl)phenothiazine, 10-(2-pyrrolidin-1-yl-ethyl)phenothiazine, 2-methoxy-10-methyl-phenothiazine, 1-methoxy-10-methylphenothiazine, 3-methoxy-10-methylphenothiazine, 3,10-dimethylphenothiazine, 3,7,10-trimethylphenothiazine, 10-(2-hydroxyethyl)phenothiazine, 10-(3-hydroxypropyl)phenothiazine, 3-(2-hydroxyethyl)-10-methylphenothiazine, 3-hydroxymethyl-10-methylphenothiazine, 3,7-dibromophenothiazine-10-propionic acid, phenothiazine-10-propionamide, chlorpromazine, 2-chloro-10-methylphenothiazine, 2-acetyl-10-methylphenothiazine, 10-methylphenoxazine, 10-ethylphenoxazine, phenoxazine-10-propionic acid, 10-(2-hydroxyethyl)phenoxazine or 4-carboxyphenoxazine-10-propionic acid.

The enhancing agents may be obtained from Sigma-

Aldrich, Janssen Chimica, Kodak, Tokyo Kasai Organic Chemicals, Daiichi Pure Chemicals Co. or Boehringer Mannheim; N-methylated derivatives of phenothiazine and phenoxazine may be prepared by methylation with methyliodide as described by Cornel Bodea and Ioan Silberg in "Recent Advances in the Chemistry of Phenothiazines" (Advances in heterocyclic chemistry, 1968, Vol. 9, pp. 321-460); B. Cardillo & G. Casnati in Tetrahedron, 1967, Vol. 23, p. 3771. Phenothiazine and phenoxazine propionic acids may be prepared as described in J. Org. Chem. 15, 1950, pp. 1125-1130. Hydroxyethyl and hydroxypropyl derivatives of phenothiazine and phenoxazine may be prepared as described by G. Cauquil in Bulletin de la Society Chemique de France, 1960, p.1049.

The enhancing agent of the invention may be present in concentrations of from 0.01 to 5000 μM, in particular of from 0.1 to 500 μM.

Brightening agents

According to the invention a brightening agent is an agent which is capable of whitening the bleached/decolourized areas of dyed fabrics. Typical brightening agents are optical brighteners and/or peroxide compounds. The brightening agent may be used alone or a mixture of two or more agents may be used, e.g., a mixture of an optical brightener and a peroxide compound.

Optical brighteners, also called optical brightening agents, or fluorescent whitening agents (FWA), are colourless dyestuffs which have the ability to absorb invisible ultraviolet radiation and retransmit it as visible, apparently white, light (for reference see "AATCC: Garment Wet Processing Technical Manual", 1994, published by American Association of Textile Chemists and Colorists, p.35).

Although the increase in brightness is nominally perceived as white, closer inspection under neutral light

sources reveals that various optical brightening agents impart a slight cast, or hue, to the bleached dyed fabric.

According to the invention useful optical brighteners are imidazol derivatives, e.g., benzimidazol derivatives, coumarin derivatives, e.g., coumarin styryl derivatives, stilbene derivatives, e.g., stilbene disulphonic acid derivatives, pyrazoline derivatives and oxazole derivatives.

Useful peroxide compounds are hydrogen peroxide or a hydrogen peroxide precursor for in situ production of hydrogen peroxide, e.g., percarbonate or perborate, or a hydrogen peroxide generating enzyme system, e.g., an oxidase and a substrate for the oxidase, or an amino acid oxidase and a suitable amino acid, or a peroxycarboxylic acid or a salt thereof.

The amount of brightening agent will vary dependent on the desired look of the fabric and the brightening agent in question but for most purposes the brightening agent in the aqueous medium is present in concentrations of from 0.01 to 100 mM, in particular in concentrations of from 0.1 to 50 mM.

Industrial Applications

The process of the present invention is typically used in industrial machines for making fabric look bleached. Normally, the process of the invention will be performed on fabric already stonewashed, but the process may also be applied to fabric which has not undergone a stonewashing process beforehand. The stonewash treatment may be performed by any treatment known in the art, typically by a pumice stone washing and/or a cellulase treatment (for reference see "AATCC: Garment Wet Processing Technical Manual", 1994, published by American Association of Textile Chemists and Colorists, pp. 19-21).

The fabric is normally added to the machine according to the machine capacity per the manufacturer's instruc-

tions. The fabric may be added to the machine prior to introducing water or the fabric may be added after water is introduced. The phenol oxidizing enzyme system and the enhancing agent of the invention may be present in the water prior to adding the fabric or they may be added after the fabric has been wetted. The phenol oxidizing enzyme system may be added simultaneously with the enhancing agent or they may be added separately. Often a buffer will be used in order to be close to the pH optimum of the enzyme. After the fabric has been contacted with the phenol oxidizing enzyme system and the enhancing agent of the invention it should be agitated in the machine for a sufficient period of time to ensure that the fabric is fully wetted and to ensure the action of the enzyme system and the enhancing agent. Typically a reaction time between 5 and 60 minutes and a reaction temperature between 20°C and 90°C, in particular between 40°C and 80°C, will be suitable.

The above described bleaching process may be performed once or it may be repeated two or three times depending on how bleached the dyed fabric should look. Instead of making one bleaching of 60 minutes length it may often be advisable to make two bleaching processes each lasting 30 minutes.

The brightening process may be carried out simultaneously or after the bleaching process. The brightening agent of the invention may be present in the water prior to adding the fabric or it may be added after the fabric has been wetted. The brightening agent will typically be dissolved in a buffer depending on the optimal pH of the brightening process. The reaction time and the reaction temperature vary depending on the wanted look and the brightening agent in question. Typically a reaction time between 5 and 60 minutes and a reaction temperature between 20°C and 90°C, in particular between 40°C and 80°C, will be suitable.

The invention is further illustrated in the following examples which are not intended to be in any way limiting to the scope of the invention as claimed.

EXAMPLE 1

Bleaching and brightening of indigo dyed denim.

Fabric: The following denim fabrics were bleached and brightened according to the invention:
Swift® denim fabric,
sulphur-bottom denim from Cone mills, USA, and
Levis jeans, type 501.
Before the bleaching process the denim fabrics were "Stone-washed" according to following procedure:

A 12 kg Wascator FL 120 wash extractor using 40 liters of water was used for stone-washing 3.2 kg of denim fabric.

Denim load:	3.2 kg
Water:	40 l
Buffer:	30 g KH_2PO_4
	10 g Na_2HPO_4
pH:	6.8
Enzyme:	70 g Denimax™ T (a commercial product available from Novo Nordisk A/S, Bagsvaerd, Denmark)
Time:	2 hours
Temperature:	55°C

Bleaching:
Bleaching was subsequently carried out in the same wash extractor using 40 liters of water and 1.6 kg of denim fabric, previously treated with cellulase as described above.

Enzyme: Laccase derived from *Trametes villosa* (SP 504, available from Novo Nordisk A/S) was used.

The following conditions were applied:

Denim load:	1.6 kg
Water:	40 l
Buffer:	105 g $(NH_4)_2SO_4$
	25.5 g $NaHSO_4$
pH:	6.5
Enzyme:	4000 LACU (laccase)
Enhancing agent:	2.7 g phenothiazine-10-propionic acid
Time:	30 minutes
Temperature:	60°C

Brightening:

Brightening too was carried out in the Wascator, again using 40 liters of water. Conditions were as follows:

Denim load:	1.6 kg
Water:	40 l
Buffer:	0.5 g/l Na_2CO_3
pH:	9.5
Optical brightener:	16 g Blankophor BA liquid (a commercial product available from Bayer AG, Germany)
Time:	15 minutes
Temperature:	70°C

Evaluation: The results were evaluated visually in a lightbox as well as by measuring the reflection. For the latter a

Texflash 2000 (available from Datacolor) was used to evaluate the degree of bleaching and brightening using the change in the color space coordinates $L^*a^*b^*$:

L gives the change in black ($-L^*$)/white ($+L^*$), a gives the change in green ($-a^*$)/red ($+a^*$), and b gives the change in blue ($-b^*$)/yellow ($+b^*$).

A decrease in L^* means an increase in blackness (decrease of white colour), an increase in L^* means an increase in whiteness (a decrease in black colour), a decrease in a^* means an increase in green colour (decrease in red colour), an increase in a^* means an increase in red colour (a decrease in green colour), a decrease in b^* means an increase in blue colour (a decrease in yellow colour), and an increase in b^* means an increase in yellow colour (a decrease in blue colour).

The bleached and brightened stone-washed denim swatches were compared to non-treated stone-washed swatches.

The Texflash 2000 was operated in the $L^*a^*b^*$ coordinate system. The light source used was a CIE light standard C. Each measurement was an average of 10 measurements. The instrument was calibrated using calibration plates (black and white).

Results

The results are presented in Table 1, which shows $L^*/a^*/b^*$ of the three denim types upon bleaching and brightening. $\Delta(L^*/a^*/b^*)$ for the bleaching and for the brightening step is calculated.

Table 1

Type of denim	Process step	L^*	a^*	b^*	ΔL^*	Δa^*	Δb^*
Swift	Stone-washing	28.34	-0.84	-19.02			
	Bleaching	46.8	-3.49	-15.90	18.46	-2.65	3.12
	Brighten-ing	47.53	-0.36	-23.03	0.73	3.13	-7.13
Cone mill	Stone-washing	33.76	-1.70	-15.95			
	Bleaching	49.99	-3.04	-10.44	16.23	-1.34	5.51
	Brighten-ing	52.07	-0.45	-16.67	2.08	2.59	-6.23
Levis 501	Stone-washing	35.82	-2.20	-15.39			
	Bleaching	55.44	-2.78	-7.35	19.62	-0.58	8.04
	Brighten-ing	56.26	-0.38	-15.40	0.82	2.40	-8.05

From the results presented in Table 1, as well as from the visual evaluation, it can be concluded that

1) A significant bleaching is obtained in the bleaching step (indicated by the change in L^*).

2) The bleaching causes a shift in a^* and b^* in the direction of a more green and yellow shade, respectively.

3) The subsequent brightening has an effect on a^* and b^* in the opposite direction as the bleaching. That is, the greyish and yellowish look of the denim after the bleaching is strongly reduced by the brightening.

By carefully selecting the type and dosage of brightening agent, it is possible to obtain any look and shade between that of denim only bleached with enzyme + enhancing agent and that of denim bleached and subsequently thoroughly brightened. The latter is similar to the look and shade obtained by a traditional hypochlorite bleaching process.

EXAMPLE 2

Similar to Example 1, except that the brightening was carried out by 3 consecutive launderings with a common household detergent containing optical brightener (Ariel Futur).

The results on Swift denim is shown in the following table (Table 2):

Table 2

Process step	L^*	a^*	b^*	ΔL^*	Δa^*	Δb^*
Stone-washing	28.34	-0.84	-19.02			
Bleaching	46.8	-3.49	-15.90	18.46	-2.65	3.12
Brighten-ing	48.59	-0.49	-22.15	1.79	3.0	-6.25

From the results presented in Table 2, as well as from the visual evaluation, it can be concluded that

1) A significant bleaching is obtained in the bleaching step (indicated by the change in L^*).

2) The bleaching causes a shift in a^* and b^* in the direction of a more green and yellow shade, respectively.

3) The subsequent brightening has an effect on a^* and b^* in the opposite direction as the bleaching. That is, the greyish and yellowish look of the denim after the bleaching is strongly reduced by the brightening.

4) The effect achieved with the optical brightener of Ariel Futur is approximately the same as the effect achieved with Blankophor BA as described in Example 1.

EXAMPLE 3

Brightening with per-acids

Fabric, abrasion and bleaching: Swift denim fabric (type Dakota) was abraded and bleached as described in Example 1, except that a lower dosage of laccase and enhancing agent were applied in the bleaching step:

2.0 g enhancing agent and
2000 LACU laccase

Brightening:

Brightening was carried out in the Wascator at following conditions:

Denim load:	1.6 kg
Water:	40 l
Buffer:	0.5 g/l Na_2CO_3
pH:	9.5
Brightening agent:	120 g Sodium perborate or 80 g Sodium percarbonate or 120 g Sodium persulfate
Time:	15 minutes
Temperature:	60°C

Evaluation:

Similar to Example 1.

Results:

The results are shown in the following table (Table 3):

Table 3

Process step	L^*	a^*	b^*	ΔL^*	Δa^*	Δb^*
Abraded and bleached	38.38	-3.21	-16.71			
Brightening with perborate	39.81	-2.85	-17.35	1.43	0.36	-0.64
Brightening with percarbonate	39.73	-2.94	-17.65	1.35	0.27	-0.94
Brightening with persulfate	40.58	-2.93	-17.28	2.20	0.28	-0.57

As also seen in Examples 1 and 2, the brightening causes an increase in a-value and a decrease in b-value. However, as opposed to brightening with optical brighteners the major effect of brightening with per-acids is on the L-value. From visual evaluation the brightening with all 3 different per-acids resulted in denim with a "cleaner" (more brightened) look, i.e. an increased contrast was obtained.

CLAIMS

1. A process for providing a bleached and brightened look in the colour density of the surface of dyed fabric, the process comprising

(a) contacting, in an aqueous medium, a dyed fabric with a phenol oxidizing enzyme system and an enhancing agent;

(b) simultaneously or subsequently treating said fabric with a brightening agent.

2. A process according to claim 1, wherein the fabric is dyed with a vat dye.

3. A process according to claim 2, wherein the vat dye is indigo or thioindigo.

4. A process according to claims 1-3, wherein the fabric is a cellulosic fabric or a mixture of cellulosic fibres or a mixture of cellulosic fibres and synthetic fibres.

5. A process according to any of claim 4, wherein the fabric is denim, preferably denim dyed with indigo or thioindigo.

6. A process according to claim 1, in which the phenol oxidizing enzyme system is a peroxidase and a hydrogen peroxide source.

7. A process according to claim 6, wherein the peroxidase is horseradish peroxidase, soybean peroxidase or a peroxidase enzyme derived from *Coprinus*, e.g. *C. cinereus* or *C. macrorhizus*, or from *Bacillus*, e.g. *B. pumilus*, or *Myxococcus*, e.g. *M. virescens*.

8. A method according to claim 6 or 7, wherein the hydrogen peroxide source is hydrogen peroxide or a hydrogen peroxide precursor, e.g. perborate or percarbonate, or a hydrogen peroxide generating enzyme system, e.g. an oxidase and its substrate, or a peroxycarboxylic acid or a salt thereof.

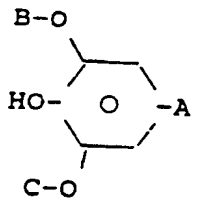
9. A method according to claims 1-8, wherein the aqueous medium contains H_2O_2 or a precursor for H_2O_2 in a concentration corresponding to 0.001-25 mM H_2O_2.

10. A process according to claim 1, in which the phenol oxidizing enzyme system is a laccase or a laccase related enzyme together with oxygen.

11. A process according to claim 10, wherein the laccase is derived from *Trametes*, e.g. *Trametes villosa*, *Coprinus*, e.g. *Coprinus cinereus*, or Myceliophthora, e.g., Myceliophthora thermophila.

12. A process according to claims 1-11, wherein the concentration of the phenol oxidizing enzyme corresponds to 0.001-100 mg of enzyme protein per liter of aqueous medium.

13. A process according to claims 1-12, wherein the enhancing agent can be described by the following formula:

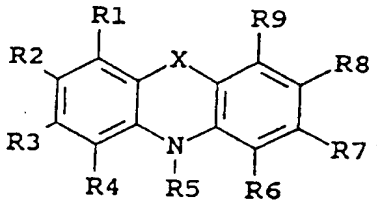


in which formula A is a group such as -D, -CH=CH-D, -CH=CH-

CH=CH-D, -CH=N-D, -N=N-D, or -N=CH-D, in which D is selected from the group consisting of -CO-E, -SO_2-E, -N-XY, and -N^+-XYZ, in which E may be -H, -OH, -R, or -OR, and X and Y and Z may be identical or different and selected from -H and -R; R being a C_1-C_{16} alkyl, preferably a C_1-C_8 alkyl, which alkyl may be saturated or unsaturated, branched or unbranched and optionally substituted with a carboxy, sulfo or amino group; and B and C may be the same or different and selected from C_mH_{2m+1}; $1 \leq m \leq 5$.

14. A process according to claim 13, wherein the enhancing agent belongs to the group consisting of acetosyringone, syringaldehyde, methylsyringate and syringic acid.

15. A process according to claims 1-12, wherein the enhancing agent can be described by the following formula:



in which formula X represents (-O-) or (-S-), and the substituent groups R^1-R^9, which may be identical or different, independently represents any of the following radicals: hydrogen, halogen, hydroxy, formyl, carboxy, and esters and salts hereof, carbamoyl, sulfo, and esters and salts hereof, sulfamoyl, nitro, amino, phenyl, C_1-C_{14}-alkyl, C_1-C_5-alkoxy, carbonyl-C_1-C_5-alkyl, aryl-C_1-C_5-alkyl; which carbamoyl, sulfamoyl, and amino groups may furthermore be unsubstituted or substituted once or twice with a substituent group R^{10}; and which phenyl may furthermore be unsubstituted or substituted with one or more substituent groups R^{10}; and which C_1-C_{14}-alkyl, C_1-C_5-alkoxy, carbonyl-C_1-C_5-alkyl, and aryl-C_1-C_5-

alkyl groups may be saturated or unsaturated, branched or unbranched, and may furthermore be unsubstituted or substituted with one or more substituent groups R^{10};

which substituent group R^{10} represents any of the following radicals: halogen, hydroxy, formyl, carboxy and esters and salts hereof, carbamoyl, sulfo and esters and salts hereof, sulfamoyl, nitro, amino, phenyl, aminoalkyl, piperidino, piperazinyl, pyrrolidino, C_1-C_5-alkyl, C_1-C_5-alkoxy; which carbamoyl, sulfamoyl, and amino groups may furthermore be unsubstituted or substituted once or twice with hydroxy, C_1-C_5-alkyl, C_1-C_5-alkoxy; and which phenyl may furthermore be substituted with one or more of the following radicals: halogen, hydroxy, amino, formyl, carboxy and esters and salts hereof, carbamoyl, sulfo and esters and salts hereof, and sulfamoyl; and which C_1-C_5-alkyl, and C_1-C_5-alkoxy groups may furthermore be saturated or unsaturated, branched or unbranched, and may furthermore be substituted once or twice with any of the following radicals: halogen, hydroxy, amino, formyl, carboxy and esters and salts hereof, carbamoyl, sulfo and esters and salts hereof, and sulfamoyl;

or in which general formula two of the substituent groups R^1-R^9 may together form a group -B-, in which B represents any of the following the groups: $(-CHR^{10}-N=N-)$, $(-CH=CH-)_n$, $(-CH=N-)_n$ or $(-N=CR^{10}-NR^{11}-)$, in which groups n represents an integer of from 1 to 3, R^{10} is a substituent group as defined above and R^{11} is defined as R^{10}.

16. A process according to claim 15, wherein the enhancing agent belongs to the group consisting of 10-methylphenothiazine, phenothiazine-10-propionic acid, phenoxazine-10-propionic acid, phenoxazine-10-hydroxyethyl, phenothiazine-10-ethyl-4-carboxy, promazine hydrochloride and phenothiazine-10-ethylalcohol.

17. A process according to claims 1-16, wherein the

enhancing agent in the aqueous medium is present in concentrations of from 0.01 to 5000 μM.

18. A process according to any preceding claim, wherein the brightening agent belongs to the group consisting of imidazol derivatives, coumarin derivatives, stilbene derivatives, pyrazoline derivatives and oxazole derivatives.

19. A process according to any preceding claim, wherein the brightening agent is a peroxide compound.

20. A process according to claim 19, wherein the peroxide compound is hydrogen peroxide or a hydrogen peroxide precursor for in situ production of hydrogen peroxide, e.g., percarbonate or perborate, or a hydrogen peroxide generating enzyme system, e.g., an oxidase and a substrate for the oxidase, or an amino acid oxidase and a suitable amino acid, or a peroxycarboxylic acid or a salt thereof.

21. A process according to claims 1-20, wherein the brightening agent in the aqueous medium is present in concentrations of from 0.01 to 100 mM.

22. A fabric obtainable by the process according to claim 1.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/DK 97/00003

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: D06M 16/00, D06L 3/02, C11D 3/386, D06P 5/02
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: D06M, D06L, C11D, D06P

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 9533040 A1 (THE PROCTER & GAMBLE COMPANY), 7 December 1995 (07.12.95) --	1-22
X	WO 9533042 A (THE PROCTER & GAMBLE COMPANY), 7 December 1995 (07.12.95) --	1-22
X	WO 9412619 A1 (NOVO NORDISK A/S), 9 June 1994 (09.06.94) --	1-22

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"B" erlier document but published on or after the international filing date
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
24 April 1997	07.05.97
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Solveig Gustavsson Telephone No. +46 8 782 25 00

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

02/04/97

International application No.
PCT/DK 97/00003

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9533040 A1	07/12/95	NONE	
WO 9533042 A	07/12/95	EP 0763095 A	19/03/97
		US 5445755 A	29/08/95
WO 9412619 A1	09/06/94	CA 2150564 A	09/06/94
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		FI 952646 A	31/05/95
		JP 8503370 T	16/04/96

98-329014/29 D16 F06 HOWA-96.10.11
HOWA KK *JP 10121387-A
96.10.11 96JP-270034 *(98.05.12)* D06P 5/13, 1/50, 3/60

Method for decolouring fibrous dyed products - comprises reducing the fibrous dyed product of woven fabric by using a saccharide having reducing powder

C98-101756

The method comprises reducing the fibrous dyed prod. (DP) of woven fabric or its sewed prod. by using a saccharide (SA) having reducing power to decolour.

USE

The method is used for forming an used like appearance of (DP) of cellulose fibre, e.g. denim, etc.

ADVANTAGE

The method can give comfortable feel to human skin and to environmental condition.

PREFERRED COMPONENT

(SA) can be a saccharide formed from decomposition of cellulose fibre by enzyme for decreasing work of cellulose fibre in (DP).

D(5-A2C, 5-C8) F(3-B, 3-F14)

PREFERRED CONDITION

The method can be pref. normally dyeing (DP), and adding (SA) together with a desizing agent (DA) into one bath in desizing process to give desizing and the decolouring by reduction in one bath simultaneously.

(5pp098DwgNo.0/3)

JP 10121387-A